Contribution

to the

Knowledge of the Chemistry of the Crystalline Aggregates.

Inaugural-Dissertation

der

hohen philosophischen Fakultät II
der Universität Bern

zur

Erlangung der Doktorwürde

vorgelegt von

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Vereinigte Staaten.

BERN
Buchdruckerei Hans Schenk
1929

Angenommen von der Fakultät auf Antrag des Herrn Prof. Dr. V. KOHLSCHÜTTER.

Bern, den 19. Februar 1929.

Der Dekan:
Prof. **S. Mauderli.**

R. UNIV.
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LEIDEN

I take this occassion to express my thankfulness for the guidance in this work of

Professor Dr. V. Kohlschütter

and who has been instrumental in the development of my knowledge of chemistry.

Wm. A. Endriss.

Dedicated
to the memory of my father, and to
patience and foresight of my mother.

The chemistry of the chrystalline aggregates.

Introduction.

1. This work continues the researches made by Labanukrom (Inaugural dissertation, Berne 1928) and treats as that research, a field, which can be called the »chemistry of crystalline aggregates«. The separation of this field is given thru the observations that matter continously appears in a kind of grouping, or under certain conditions, as microscopical or macroscopical crystalline combinations, which enables one often to recognize their special nature or to know the conditions under which they became so, and even cause the real interest of the material. Countless examples of this can be found in mineralogical examples of certain compounds and in inorganic precipitates from the body or in different manufactured products.

The appearance of the forms in question is due to, on one hand to the nature of the material and on the other hand to the conditions under which they are made. Because of this they can be called a physical chemical problem and from this one can speak of a chemistry of aggregate forms. The problem of chemistry is really to describe the material according to its characteristic properties and its behavior under certain physical or chemical circumstances.

2. The material of observation in this field is very large, but it has been found accidently or supplementary to other thoughts. There has been very little systematic work done to obtain the reasons for the formation of such typical aggregates.

In this institute Labanukrom recently made researches on a group of substances, which appeared to be especially suited for such observations under different view-points. These were basic copper salts.

These compounds are, more complicated than the ordinary binary salts, but if they are regarded as complex compounds they are relatively simple and appear to be made up of a similar complex form. They are not soluble and can be precipitated from solution by a unified process which gives characteristic crystal forms. These forms are very small and for their examination high-power objectives must be used which as we shall explain later was not disadvantageous.

Labanukrom has been able to gather a large quantity of useful material. He showed that in using the same method of preparation with different anions one can get well developed individual crystals, some of which are isomorphic and similar in their habitus. Noticeable too is that they have generally a thin tabular form. Besides these crystalline forms they appear as aggregates which differ from one compound to the other. Often there is only one kind of structure known in which that compound can be used as a means of indentification of that salt.

3. A number of reasons why these aggregates are formed can be had by observing the objects themselves, or noticing the conditions under which they were formed.

Most of Labanukrom's researches were that he aided the hydrolysis of simple copper salts thru the addition of urea and also by increasing the temperature above that of the room. As urea is a very weak base, the OH' concentration can be held at a fairly constant value. Thru the immediate use of the hydroxyl, which is delivered in a steady but small concentration, the basic copper salt formed. The reaction goes slowly not only because of the time necessary for the progress of the hydrolysis but also as a complex formation. The formation of the germination center and its development into crystals and aggregates takes place anywhere in the solution but is especially favored along the walls so that not only larger quantities may be had as sediment at the bottom of the container but also on object-glasses which have been placed therein, making very useful microscopial preparations.

4. The formation of basic salts can be brought about, as is well known, by the insufficient addition of alkali to Cu-solutions but the products here, are not well formed nor are they uniform.

Besides the methods mentioned for the preparation of basic copper salts a second still more satisfactory and often used preparative method was used. This method uses copper hydroxide and treats it with solutions of copper salts.

As long as pure copper salts are used, this method has this in common with the hydrolysation method, that the copper hydroxide is not present in any great concentration for the for-

mation of the chemical complex, but is given slowly and in small, quickly used portions from the sediment in the container. This is true, at least if one accepts the fact that a molecular process is going on in the solution. It differs from the hydrolysation method in that the reaction is bound more or less on a solid or gel-like material. For this reason the reaction is to be included in the topochemical processes and one may ask how far one has to consider the process as going over the solution and what is the influence that confinement of place has on the reaction and the product.

Thru the interaction of alkali (or alkali-earth) salts with copper hydroxide or thru the treatment of a solution of copper hydroxide with an insufficient quantity of acid one can get basic salts. The reaction of metallic salts on copper hydroxide leads us further, as it can be used for the formation of an interesting class of basic copper salts with two different kinds of metallic atoms.

5. Our knowledge about such double basic salts is given in the researches of Sabatier (Comptes Rendus Vol. 125, p. 101, 175 and 301 also vol. 129, p. 211 vol. 132b, p. 1538) and mainly A. Maihle (Comptes Rendus vol. 132b, p. 1273, 1538, 1560; vol. 134, p. 34, and vol. 134a, p. 233); and also work of A. Recoura (Comptes Rendus vol. 132b, p. 1414). Thoughts over their constitution has been given by Werner (Ber. vol. 40d, p. 4441, [1907]). The latter — says if the copper compounds with only copper atoms of the formula CuX_2 $3Cu(OH)_2$ are especially observed — they can be regarded as salts of this type $[Cu(H_2O)_6]\ X_2$ called by him »hexol« salts, in which the 6 molecules of H_2O can be displaced by 3 molecules of $Cu(OH)_2$, or as metallic salts which have added a trimolecular $Cu(OH)_2$ i. e. $Cu(OH)_2 \cdot CuX_2$.

With such a view-point one can well imagine that this trimolecular $Cu(OH)_2$ can be added as an entirety to other metallic salts whereby compounds of the type given by Maihle (Ann. chim. phys. vol. 7, p. 362 [1902]) could appear . . . . . .

Werner

$$Cu_2(OH)_4 \cdot Cu\begin{matrix} OH \\ \\ OH \end{matrix} ZnCl_2 + 1H_2O$$

Maihle

$$M''Cl_2 \cdot 3CuO \cdot 4H_2O$$

$Cu_2(OH)_4 \cdot Cu\begin{matrix}OH\\ \\ OH\end{matrix}Zn(NO_3)_2$ $\qquad$ $M''(NO_3)_2 \cdot 3CuO \cdot 3H_2O$

$Cu_2(OH)_4 \cdot Cu\begin{matrix}OH\\ \\ OH\end{matrix}ZnSO_4 + XH_2O$ Various formulas according to the salt made.

X is either 2 or 9.

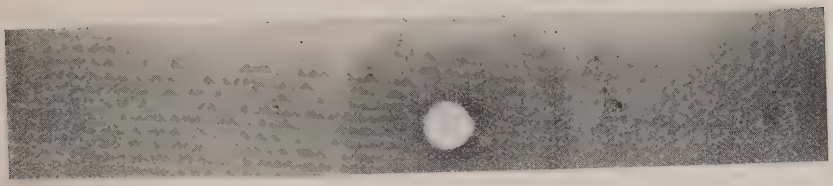
These double atomic salts are related to each other according to the data of Maihle, that they are isomorphic. As an example, he states that the nitrates and $3Cu(OH)_2 \cdot Cu(NO_3)_2$ (Gerhardtit) are isomorph, and of the bromides those with Zn, Co, Ni are also isomorph and also the sulphates of Co and Ni. According to Werner one can clearly see that this trimolecular $Cu(OH)_2$ can take a part in the formation of complex compounds as a simple metallic hydroxide. He goes even further and claims that because of this the metallic hydroxides as $Cu(OH)_2$ are seldom able to appear in the monomolecular form.

6. As logical as these systematic observations may be, there is no proof for the constitution and it can only be completed after the use of X-ray pictures, but so far there are still a number of difficulties in the interpretation of such pictures. Then too one is not able to say much, for the time being, over the real mechanics of their formation from $Cu(OH)_2$ and metallic salts as there are quite a number of possibilities.

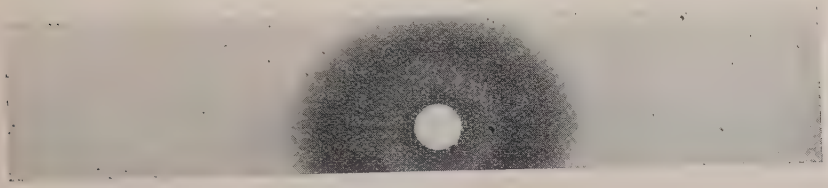
In order to get certain pointers in these questions, a number of conductivity determinations were made during their formation and also the effect of alkali salts on hydroxide. Even though several interesting facts were found, the questions were not definitely decided, and will not be referred to, as the conditions are complicated enough as they are.

We hoped however to be able to gather some experience thru the examination of their forms and their development thru the reaction on solid hydroxide and also something over their mechanics. Nevertheless one could expect, thru a comparison with the products of other methods to infer something from the forms there, about how they came to be. In this relation too, a comparison of the single atomic basic salts with the forms of the mixed atomic salts, would be interesting. To get material for this comparison, should be my main problem.

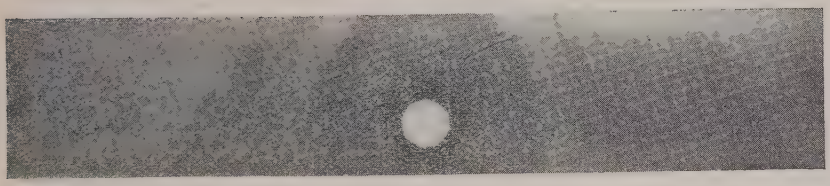
X-Ray Diagrams.



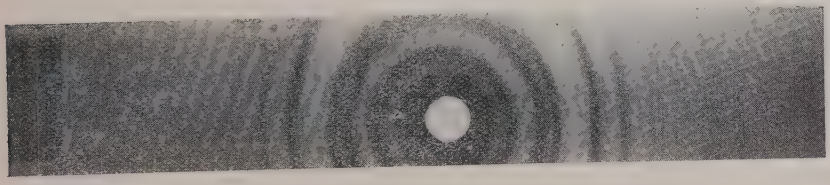
$Cu(OH)_2$ Freshly made; A type.



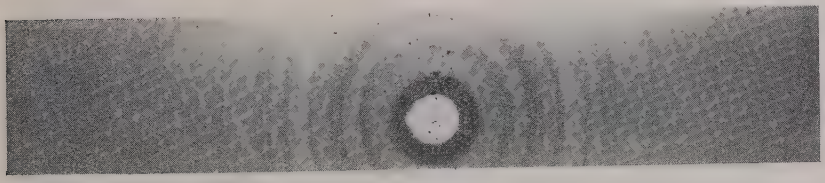
Aged hydroxide; B type.



Frozen hydroxide; C type.



Crystalline hydroxide from basic nitrate; D type.



Basic copper nitrate.

7. The general method of procedure used by me, was to treat pure copper hydroxide with a solution of metallic salts.

As a continuation of the researches of Labanukrom the reaction of copper salts on hydroxide was used, and in order to complete the thought, the reaction of hydroxide with free acids for there was a possibility that the localisation of the reaction would differ from the hydrolysis of dissolved salts, which is a process in space. After this metallic salts with other cations were brought into the reaction. The researches were confined mostly to the sulphate, nitrate and chloride and as second cation Co, Ni, Zu, Cd and Ag were used.

The work was carried out purposely at ordinary temperatures. Maihle emphasized that the reaction of hydroxide with metallic salts gives the same product regardless whether one work with or without heat, only that with heat, the reaction is proportionally quicker. A difference is however present in that the higher temperature of the solution helps the appearance and development of the individual crystals, and also that unified products are obtained. For us the important fact was to have the reaction most subtile and to observe all the fine effects. The formation is more sensitive at ordinary temperature, while they are lost at higher temperatures. In consideration of the interest that all morphological studies have for the formations in the cells and organisms the keeping of ordinary conditions of life is very much desired.

The limitation of the temperature range is also due to the fact that an analytical study of the product was omitted although efforts were made in this direction. Scientists have shown that it is hard to get sure results in the basic copper salts. The exact microscopical observation of the products in which very characteristic reproducible pecuilarities were present showed us repeatedly how useless their analysis would be, because they were not uniform, also researches from the view-point of the phase theory, which appears to give the greatest prospects and which has been taken up recently again meets unsurmountable difficulties, because of the very noticeable and great stability of the once formed bodies and the setting in of the equilibrium does not take place within a reasonable time.

For this reason we have held ourselves mainly to microscopical and microchemical observations and again it was only with the help of the high power objectives that we could find typical appearances.

This has various advantages:

First, the size of the formed body is relatively small at these dimensions. Because of the size, the form receives a greater impression of the factors which are most effective for its formation, than if the forms had developed to a large size. Or in other word one can say that the space for the formation is closely bounded and this helps the dynamics and structure to be impressed on the forms.

Second, the characteristic development of the forms is more pronounced on small bodies than when the aggregates are large and the details and parts can be better observed to the border of human visibility and a general view can better be had over the whole.

A variation of the conditions within the same system ($Cu(OH)_2$ — metallic salt) was obtained at first by the use of various concentrated solutions. On the whole, from our own experiences and especially those of Maihle, we have kept ourselves in a concentration there the same compound is formed with a possible exception with zinc sulphate. Within this concentration range there was generally found one developed form which could be regarded as typical for that compound. The characteristic form appears often in all concentrations equally developed only that their size varies. In other cases the characteristic form is found within a close border and changes more or less as a slight variation to the right or left of the most favored solution is made.

The most important change in the conditions was caused by the use of different kinds of copper hydroxide.

We used four kinds of hydroxide which will be regarded in the following discussions as A, B, C, and D. They are marked according to their method of preparation. A closer description of their form is given in the experimental part. These are as follows:

A. is a freshly made very pure and active blue gel, which was used as a water suspension.

B. is a product obtained from A, changing into CuO at ordinary temperature and is a colloidal suspension of it.

C. is a product also obtained from A by freezing and is a sharp cornered spittered mass.

D. is hydroxide of the exact composition $Cu(OH)_2$ which is a true pseudomorphic variety of the basic nitrate and which has been obtained thru topochemical change with NaOH and afterward throughly washed.

A chemical and morphological description of these forms has already been partially given by Sedelinovich (Z. E. Chemie, vol. 29, p. 30 [1923]) and Teuscher (Z. anorg. chem., vol. 111 [1920], p. 213). The examination of them has been in the meantime conducted further; and will be mentioned in another place, but the knowledge gained from it has been used by us in judging my researches. Important for the time being is that A when freshly made gives the appearance of being an unarranged colloid probably large micells containing a lot of water. But during the time of preparation a certain arrangement takes place into a lengthwise structure which develops elongated $Cu(OH)_2$ particles. At the same time as this ageing, and partially overlapping it, is the dehydration. The result of these two processes is our B; a colloidal material, of very fine CuO particles embedded in a more or less arranged gel mass of $Cu(OH)_2$ particles. C has the appearance of being a gelatinous skin of not completely arranged hydroxide, which was pushed together thru dehydration and pressure. The reason for this thought is that a variety can be gotten if the A form with the electrolyte in which it was made i. e. without washing A, is frozen. Then one can observe, that in place of the sharp cornered splittered material, mostly small irregularly formed strands. The presence of the electrolyte affects, thru its coagulation effect, this splitting up of the material. The ability to react diminishes from A to C but is however still present; the change to CuO can be quickened thru traces of $(OH)'$. The form D pseudomorphic to the basic nitrate can be regarded as »mosaic« crystals and show a

certain dispersity but the $Cu(OH)_2$ particles are all arranged. It shows the optical properties of uniform crystals. The ability to change into CuO has disappeared completely in D.

Experimental.

1. Preparation of Copper Hydroxide.

In the chemical literature many forms of copper hydroxide may be found. We have selected two colloidal forms, one aggregate form, and one crystalline form. Before going into the experimental part of this work, the method of preparation of each will be explained.

A. A gelatinous copper hydroxide was made according to the method of R. Lorenz (Z. f. anorg. Chemie, vol. 12 [1896], p. 426). Use was made of the arrangement of Kohlschütter and Sedelinovich (Z. f. Elektrochemie, vol. 29 [1923], p. 30) in the preparation of this copper hydroxide. Into a rectangular glass container 100 cc. of n/2 or n/4 KNO_3 was added. The electrolysis was made with two copper electrodes, having 20 sq. cms. in the electrolyte, and with a current of 1 ampère, or 0,5 ampère. During the electrolysis, which lasted 5 or 10 minutes, the liquid was constantly stirred. Immediately afterwards the hydroxide was washed by filtration thru a porous Jena glass gooch crucible, until there was only 20 cc. of liquid with the hydroxide, whereupon 80 cc. of boiled distilled water was added and the filtration repeated. This crucible was kept cool by cold running water. After five complete washings there should be, theoretically from the n/2 solution, a n/6250 solution of KNO_3. Such a hydroxide was flaky, slimy blue-green gel and used immediately.

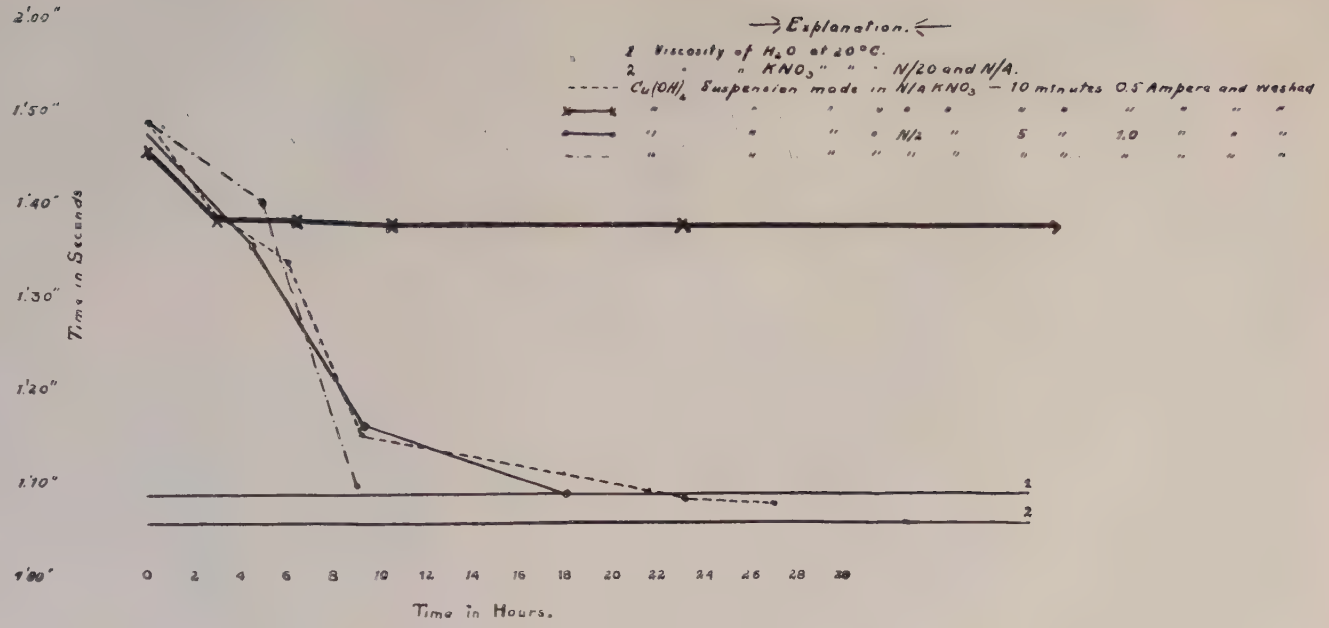
B. Our second colloidal form was a copper hydroxide which had been allowed to stand and had become partially CuO and brown in colour. It will be called »oxide« hereafter. The preparation was otherwise exactly the same as that described in the preceding paragraph. The time that such a preparation stood varied a little and we did not hold ourselves to any definite period, using it a day after the preparation. This oxide is no longer flaky but a coarse sol, which shows, under the ultramicroscope a lively Brownian movement. It settles slowly, taking

often weeks, and if it is stirred becomes a complete suspension which passes thru the filter paper. It is probably a »mixed body« of stabilized aged $Cu(OH)_2$ A or CuO in an internal colloidal mixture, because it is not possible to separate it by centrifugal or the electrophoretic proccesses. Thus it can be used as a body with a definite form. According to Sabatier (Comptes Rendus, vol. 125, p. 101) if $Cu(OH)_2$ A is heated to 100 it is 4 CuO· H_2O but this is not probable.

Vicosity determinations were made with the A gel during the time that it became brown. These determinations were made at 20^0 C. The time that water and N/4 or N/2 KNO_3 solutions are taken as a basis, accidently one obtains a gel which is stabile for a long time. Such a gel contains very little of the electrolyte and only a drop of very dilute alkali is sufficient to change the color of the gel noticeablly within five minutes. On the graph can be seen that in twenty hours the vicosity is like that of water or very close to it, except in the stabilized gel.

C. According to Villiers (Comptes Rendus vol. 120 (1895) -. 322.) »crystalline« copper hydroxide can be made by freezing the hydroxide. This was another form that was used for the experimental work. Copper hydroxide was made with the method described from Kohlschütter and Sedelinovich, but it was only washed three times. Small portions were placed in test-tubes and held frozen for two hours, in an ice and salt mixture, then they were thawed out and used as planned. The solution freezes from the edge of the tube towards the center, but not as an uniform material but water separates from the gel and freezes itsself and at last the gel freezes as a core. If the gel gotten thru our general method of preparation was not washed or what is the same left with the electrolyte and then frozen, this frozen material did not have the same form as that which was washed. It had the appearance of strands of thread. (See photographs.)

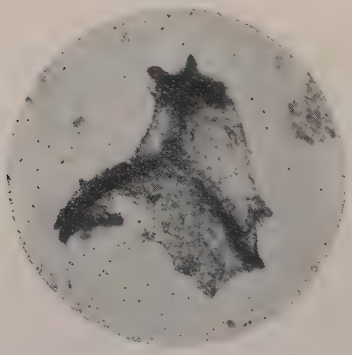
D. Another »crystalline« form was used in the research work. Kohlschütter and Teuscher (z. f. anorg. Chemie vol. 111 (1920) p. 213) made a »crystalline« hydroxide from basic copper nitrate, which was prepared from a copper nitrate and urea solution on a hot - water bath. Such a basic nitrate showed


→ Explanation. ←
1 Viscosity of H_2O at 20°C.
2 " " KNO_3 " " N/20 and N/4.
----- $Cu(OH)_2$ Suspension made in N/4 KNO_3 — 10 minutes 0.5 Ampere and washed
" " " " " " " " " " " "
" " " " N/2 " 5 " 1.0 " " "
" " " " " " " " " " " "
2'00"
1'50"
1'40"
1'30"
1'20"
1'10"
1'00"
Time in Seconds
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time in Hours.
1
2

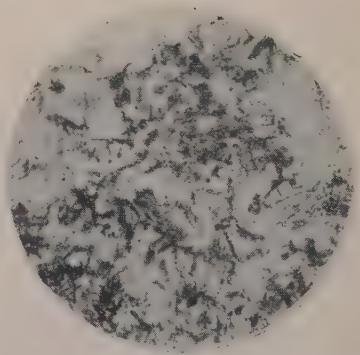
large rhombic blue-green plates. Upon treating this salt with 2N NaOH a pure blue crystalline form was obtained, which was free from nitrate.

This is a true pseudomorphic form to the basic nitrate. Its optical properties have been given by Labanukrom, and is to be regarded as a uniform crystal of the composition $Cu(OH)_2$.

Thus there were four kinds of hydroxide of which we made use of. Starting with a disperse colloidal form, thru an aged form which was no longer pure $Cu(OH)_2$, then a type in which the particles had been pressed together (Villiers' type), to a compact, arranged, pseudo-crystalline form. Regarding these forms from the time that it takes to become CuO, one has distinctive differences. The blue colloid changes rapidly into the brown form. The aged form which has been mentioned as being only partially changed to oxide, contains considerable hydroxide as Kohlschütter and Sedelinovich (Z. f. Elektrochemie, vol. 29 [1923], p. 30) have shown. The frozen hydroxide was much more stable than either of the preceding forms. It changed, however, in color very slowly in several months. Under the microscope it showed a conchoidal surface of gel pieces, and by casual observation appears to be a crystalline product and is affected by polarized light. The pseudomorphic form, from the basic nitrate is stable for an indefinite period, and the particles, in contrast to the other forms, are in a definite arrangement.



Frozen $Cu(OH)_2$ that has been washed. Magnified 360X.



Frozen $Cu(OH)_2$ with electrolyte. Magnified 360X.

With these forms of copper hydroxide we wished to see how they affected and were affected by solutions of various acids, copper salts and salts of other metals. The small quantities of hydroxide were placed, as a suspension in the test-tubes and the different solution were added. From time to time small portions were taken out with the aid of a pipette and used for the microscopical examination in order to observe the process.

The drawings were made with that combination of objective and ocular (example-objective 60X and ocular 10X=600X) which is mentioned in the drawing. However by increasing the distance from ocular to the slanting drawing table the picture was enlarged thru the Zeiss'Drawing Prism and the distance that it was from the ocular to the table. The distance from ocular to drawing table was 30 cms.

2. Reactions of Copper Hydroxide with Copper Salt.

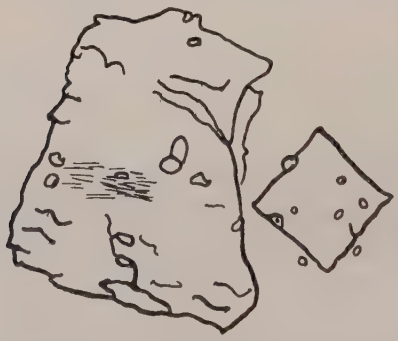
a) Copper Hydroxide with Copper Sulphate.

A. The utter inability of the colloidal hydroxide to form any definite aggregates with copper sulphate is quite noticeable. The concentration was varied between 0.33N and N solution. Because no form was noticed it does not mean that a change did not take place. A color change did take place showing that something had happened, but it was not visible at a magnification of 600X. This is no doubt a gel of basic sulphate and which Sedelinovich calls »substituted formation«. Most of the test-tubes were not corked but covered with glass crystallization dishes. As the time went on the water evaporated and the blue-green dried residue was looked at. In the 0.33N solution for instance the main part was sharp, splintery pieces. On these were small warts of basic sulphate as they were normally observed in D. Under crossed Nicols upon rotation they showed different shades while the main mass remained dark. n this splintery mass a few spindles (the typical basic sulphate form) were visible.

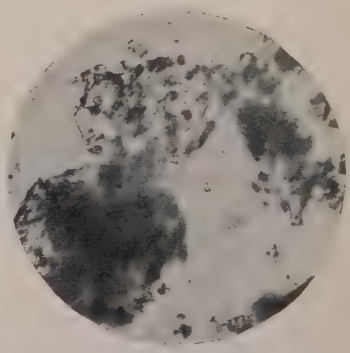
B. The frozen hydroxide was able to maintain its form in all the concentrations. It is impossible to talk of no change, because the color had become a typical pea-green. In other

words the reaction is bound to the place where the hydroxide is. The gel pieces remain for a long time and are not effected by polarized light.

C. The copper sulphate attacked the »crystalline« hydroxide in such a way at O.3N that it had a banded appearance. On the surface were little rounded globules. (See pictures.) At O.6N there were many such globules on top and close by there was some brown gel. The banded appearance had however disappeared. In a N solution the globules had decreased. The crystalline plates show unified strain figures under the polarization microscope, sharply in the concentrated solutions but not so sharp in the dilute ones. A change in the hydroxide has taken place only on the surface; special forms of the globules could not be given on the changed crystals. The globules reacted to polarized light but did not give the polarization figure, which would point to a weaker structure.



»Crystalline« $Cu(OH)_2$ in O.33N solution of $CuSO_4$. Magnified 420X.



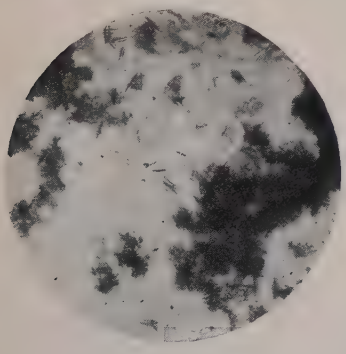
»Crystalline« $Cu(OH)_2$ with O.6N $CuSO_4$. Magnified 720X.

B. Copper hydroxide and Sulphuric Acid.

A. From the 100 cc. of hydroxide made according to the method described before, 10 cc. were treated with N/20 H_2SO_4 By titration the amount of acid necessary to exactly neutralize such a quantity was found. In the following experiments the amount of acid added was always less than the amount necessary to neutralize the hydroxide, and where $CuSO_4$ was formed at the expense of precipitate or gel of copper hydroxide.

Ten cc. of the hydroxide with 1 cc. N/20 H_2SO_4 showed at the first observation a gel and some rod-like aggregates with pyramidical ends. A week later the gel had disappeared partially and small needles were present. Another experiment with 2 cc. of N/20 H_2SO_4 showed at first needles, rod-like aggregates and gel. Later on these disappeared and very small oval forms were present. An increase to 5 cc. of acid did not give better forms but only a gel.

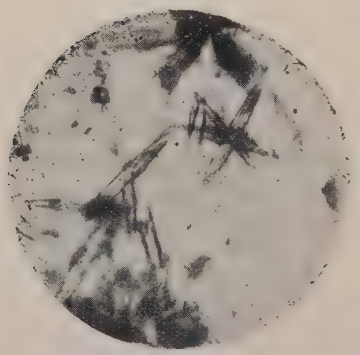
B. One cc. of this N/20 H_2SO_4 (with factor) with 10 cc. of the oxide gave at first only a brown gel, but upon examining it 5 months later the typical pointed needle forms were noticed. (See photograph.) With 2 cc. of N/20 H_2SO_4 there was at first mainly the brown gel and occasionally a few irregularly shaped forms some of which were triangular and others large crosses with elevated ridges in the center and indentations at the end. Five months later these had disappeared and the needles had taken their place. With 3 cc. of the acid the gel was still present and some forms with sharp angles. One of the shapes was like two trapezoids which had their two short sides together. Five months later the needle forms were present. With 4 cc. of the acid a non-uniform mass of shapes were present with the gel. Some of the shapes were rectangular and others star-shaped due to two triangles growing so that the angle of the one would bisect the side of the other. These shapes did not change in time.



2 cc. H_2SO_4 and CuO.
Magnified 720X.

C. The frozen hydroxide gave quite different forms than the other types had given. Upon the addition of 1 cc. of N/20 H_2SO_4 peculiar tree-like forms with gel were observed. (See photograph and drawing.) The branches were at irregular intervals. The length of a stem was 29.7μ and the width 5.4μ. The hydroxide and 2 cc. of N/20 H_2SO_4 showed under the microscope amorphic material and these tree-like forms. Their size varied and the length was measured at 29.7μ and 37.8μ and the widths

2.7μ and 13.5μ respectively. Upon the addition of 3 cc. of the N/20 H_2SO_4 the amorphic material had increased heavily and there was hardly a tree-like form. The size of them was small, being 1.3μ in width and 7.8μ in length. With 4 cc. of the N/20 acid the appearance of considerable amorphic material is noticed and some very small needles that one could hardly define. Besides this a third very small form is present looking like a rhombohedron.



Frozen CuO with 1 cc. H_2SO_4. Magnified 720X.

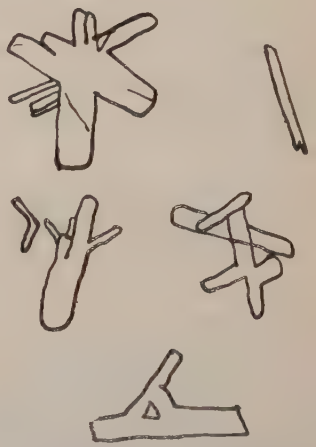


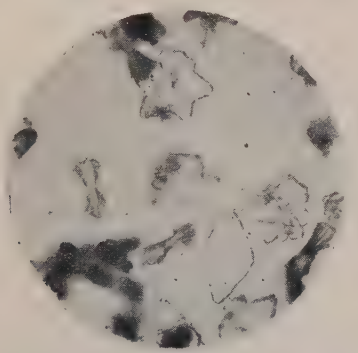
Fig. 4 Frozen $Cu(OH)_2$ with 2 cc. H_2SO_4 N/20. Magnified 600X.

D. The attack of the N/20 H_2SO_4 seems to be too strong for the »crystalline« hydroxide. The acid etches the corners and the surface, sometimes eating completely thru the crystal. The addition of more acid makes the etching more pronounced until there is nothing but a clear solution left.

In the foregoing we have only discussed the use of various quantities of acid, or in other words the use of various ratios of acid to base hydroxide. If the ratio of acid to hydroxide would be kept constant and the concentration changed we could have different conditions. With the colloidal hydroxide and the CuO experiments were made in this direction. Two ratios were selected; one with 1 cc. N/20 acid to 10 cc. of hydroxide or oxide and the other with 5 cc. N/20 H_2SO_4 to 10 cc. of hydroxide or oxide.

A. In the weak ratio of 1 cc. N/20 H_2SO_4 with the hydroxide the change was at first to a brown gel and finally a gel and needles. The time that it took was however longer in the 4 cc. N/80 H_2SO_4 than in the 1 cc. N/20 H_2SO_4. In the concentrated ratio of acid with the hydroxide the forms were rounded rods which even at 5 cc. N/20 H_2SO_4 were small and became so small with 15 cc. N/60 H_2SO_4 that they were hardly distinguishable. In none of these concentrations was there a complete absence of gel.

B. The oxide was hardly affected at first in the weak ratio of 1 cc. N/20 H_2SO_4 having mostly a brown gel and a few parallelograms. Five months later the gel was as much present as ever but the needle form had taken the place of the parallelogram form. The needles were in clusters; each form slightly



10 cc. CuO with 5 cc. N/20 H_4SO_2 showing triangles and lengthy form. Magnified 720X.

turned at an angle around a central point. The same was noticed from 2 cc. N/40 to 5 cc. N/100 H_2SO_4. The 5 cc. of N/20 acid showed quite a few double triangles with the edges indented a little. These triangular forms disappeared if they were washed and lengthy forms replaced them. (See drawings and photograph.) With 10 cc. N/40 acid the triangular forms were so arranged that they looked like a six-sided star. On the surface was quite often a round hole. Continuing the dilution to 20 cc. N/80 and 25 cc. N/100 H_2SO_4 the forms were like the preceding. After a month these triangles had disappeared and needles had appeared.

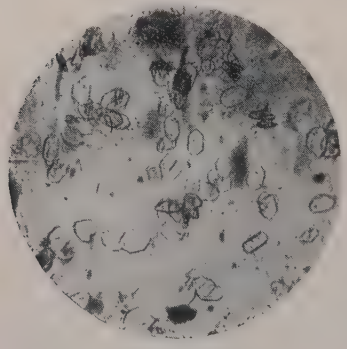
Drawing of lengthy form with Zeiss' Drawing Prism. Magnified 300 X.

100 cc. CuO with 5 cc. N/20 H_2SO_4 Drawing with Zeiss' Drawing Prism at a magnification of 300 X.

c) Copper Hydroxide with Copper Nitrate.

A. The hydroxide was treated with concentrations of $Cu(NO_3)_2$ varying between 0.25N to 9N and nothing was noticed except a gel. Under the microscope it appeared to be yellow. In 8N and 9N there was nothing but a clear solution.

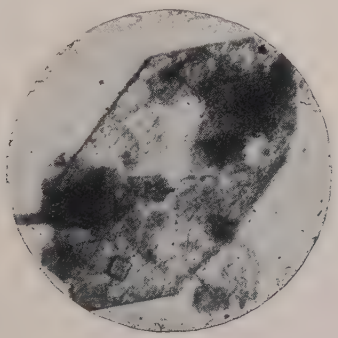
B. The naturally aged hydroxide (CuO) with various concentrations of nitrate showed quite a number of forms. In the dilute solutions the forms were about as broad as they were wide and gradually, as the concentrations increased, they became longer and narrower unitil they almost looked like needles. They had not changed upon looking at them a month later. The 0.25N solution showed elongated six-sided plates. The forms were clear. At 0.37N the rectangular form seems to have taken the upper hand. There was no gel present. Already at 0.5N the forms appeared to be clear and uniform and were longer than they were wide. They looked very much like a benzol ring and the corners were slightly rounded. At 0.75N the benzol-like forms were getting smaller and elongated. (See photograph.) This decrease in size and lengthwise increase over the width continues until 6N. Above this concentration there were no forms only a solution.



CuO with 0.75N $Cu(NO_3)_2$ Magnified 720X.

C The frozen hydroxide with copper nitrate showed in the O.25N solution small specs which had a diameter of 1.3μ to 2.6μ. These specs were not dark in any position in the polorization microscope i.e. they showed aggregate polarization. At O.5N $Cu(NO_3)_2$ the macro and micro color is about the same a blue. The specs, spoken of in O.25N, were also present. Greater concentrations did not give better forms only that the hydroxide stayed together, reacted to polarized light but not in the same manner as the hydroxide did.

D. The »crystalline« hydroxide was affected at the place where it was. In other words the original forms stood and the pseudomorphic hydroxide was changed back to the basic nitrate. from which it started. From O.25N to the 3N solution the color changes gradually from a blue to a blue-green. The macro observation gives a gradual change whereas under the microscope a crystal is either blue or blue-green, but not the two colors on the same crystal. In the dilute solutions the longitudinal lines are more than in the concentrated solutions. In the N solution and even more in the 5N and O.25N individual particles are present which show aggregate polarization. There is



»Cristalline« $Cu(OH)_2$ with N $Cu(NO_3)_2$. Magnified 720X.

at least one layer of irregular fine crystalline particles. Besides this there are newly formed small crystals on the surface of the large ones and flakes of brown gel. (See photograph.) In the 3N solution the hydroxide crystals are well defined, but have changed, at least on the surface to basic nitrate, which gives a unified strain figure.

d) Copper Hydroxide and Nitric Acid.

Ratio of acid to hydroxide varied. — *A.* To each 10 cc. of hydroxide in the test-tubes either one, two, three, or four cubic centimeters of a N/20 HNO_3 were added. In the least concentrated small needles and gel were observed. This did not change within a week of making the first observation. With 2 cc. of the acid the macro appearance was a brown slime, but the micro observation showed a gel and squares with slightly truncated corners or a benzol ring form. Ten days later these forms had disappeared and only a brown slime was present. With 3 cc. of HNO_3 the macro appearance was a brown slime and under the microscope fine needles, some rectangles whose two parallel sides had saw-toothed edges from the twinning of of several benzol ring forms. In ten days all of these had disappeared except the fine needles and the gel. With 4 cc. of this acid the macro color was a dirty green; under the microscope gel, needles and rods with a slight stricture at the center, were present. Occassionally these rods grew like a V, two having a common base. The addition of 5 cc. N 20 HNO_3 did not give these rods but only fine needles, alone or in groups.

B. One pecuilarity is that the CuO does not show the same ability to react as the hydroxide, The brown gel remains even upon later observations except where 5cc. N 20 HNO_3 had been added and large flat plates with lengthwise lines and gel, were observed.

C. The frozen hydroxide with 2 cc. N/20 HNO_3 showed mostly a gel and blunt pyramidically ended prisms, alone and in clusters. Their length varied from 32.4μ to 45.9μ and they had a width of 4μ. Once in a while they looked like a cricket bat. They were slightly affected by polarized light. With 3 cc. N/20 HNO_3 the frozen form was still present in shape and besides a form like two pencils of unequal length placed parallel. In the preceding the macro color was brown, and in this the crystals were found. With 4 cc. the macro color was blue but only small specs could be seen.

D. The »crystalline« $Cu(OH)_2$ shows that the acid was much too strong for the crystals. In all they were etched, either at the edge or on the broad surface. As the concentration increased the holes on the surface were greater and more numerous, also as the etching proceeded a considerable number of lengthwise lines appeared.

Ratio constant; concentration varied. — These experiments were like those with sulphuric acid where the concentration was always decreased while the amont of acid used was the same. In the weak ratio of 1 cc. N/20 HNO_3 to 5 cc. N/100 HNO_3 with 10 cc. of the hydroxide, there were, from 1 to 5 only small dots which got so small at 5 that they were hardly visible. In the stronger ratio of 6.5 cc. N/20 HNO_3 small rectangles and some amorphic material was present. Later the amorphic material seems to have increased at the expense of the rectangles, which have disappeared some. At 7.5 cc. N/30 HNO_3 there were rods and some amorphic material. These rods were affected by polarized light, With 8.5 cc. N/35 HNO_3 to 10.5 cc. N/42 HNO_3 the rectangles got smaller and the amorphic material was also present.

The oxide acted like it did with the nitric acid where the ratio was varied. Here there were no forms and they looked under the microscope at 600X like a brown slime.

e. Copper Hydroxide and Copper Chloride.

A discussion of all the concentrations of cupric chloride from 0.33 N to 4.5 N will be taken at once with the different forms of the hydroxides. In none were distinctive forms observed. A change probally took place because the slime that resulted was a light blue-green. There can hardly be a talk of the preservation of the various kinds of hydroxide, because the oxide became a blue white slime. The frozen forms were broken up into little particles, and became a light green blue in color. The »crystalline« hydroxide with the chloride caused a breaking up of the crystals and even in one (4N) a complete solution resulted.

Hydrochloride Acid.

A. The acid with the hydroxide gave a gel at the first observation which became compacter when the second observation was made, 10 days later. However not all of the material became compactly amorph but some remained as a gel.

B. The oxide showed with 2 cc. of N 20 HCl some gel and some amorphic material which had a light blue color in the test tube. An ageing of five months did not seem to affect it. Both of the tubes containing 4 cc. and 6 cc. of N 20 HCl showed no gel, but small irregularly shaped forms. The macro color was blue.

C. The frozen form broke up into small dots when 2 cc. N/20 HCl was added. Some of these dots were in a Brownian movement. With 4 cc. of N/20 HCl there were two colors present, blue and a brown. The blue form is irregular in shape and is much more compact than the brown which is very minute, round, and in a lively Brownian movement. Six cubic centimeters of N/20 HCl broke the frozen hydroxide into very small particles, some of which had Brownian movements. The shape was irregular.

D. The »cristalline« base was slightly etched on the flat plane surface with 2 cc. N/20 HCl. With 4 cc. the crystals were attacked on the surface and small irregular almost round bodies were formed. Had the process continued for some time the whole crystal breaks up into a mass of them. Increasing the acid to 6 cc. N/20 HCl there was nothing to see except the dissolving of the crystals at the edge or on the surface with equal ability.

Summarizing the results obtained in the reaction of copper hydroxide, the following can be said:

1. Behavior towards different salt solutions. The hydroxide A undergoes a decided change, but this change does not appear to be the same in the three salts. In the sulphate and nitrate there is a complete substitution of the hydroxide gel against one of basic salt, and in the chloride there is, furthermore, a greater dispersion, a more hydrophobic material. B reacts slower. Characteristic forms are present and in the case of the sulphate, spindle types, and rectangular or hexagonal plates are formed. Upon increasing the concentration of the salt solution the forms

become smaller (especially with the nitrate) and thinner. The general impression is that the development of the individual crystal is not only aided by the slower reaction, but that in the gel mass there is more room for its development. The behavior of C is like a compressed A. The reaction product is substituted in the material that one starts with. In the sulphate this is a disperse, optically noncrystalline material, and in the nitrate as an irregular mass of very fine crystals, and in the chloride the gel pieces break up. The D hydroxide is only attacked on the surface at first, nevertheless there is a possibility (especially with the nitrate) that the reaction of the »mosaic crystal«, which was obtained from the basic nitrate, goes thru the whole crystal with the reformation of the basic salts. The attack is in a certain direction which can be observed from the etched surface of the crystals. The formation of basic salt is made over the solution on the hydroxide crystal, or on the adjoining border of the material in the concentrated solution. The fine crystals are arranged in orderly fashion and the whole layer shows a uniform strain figure under the polarization microscope. In dilute solutions where the new formation is not so closely bound to the starting material and where the forms have been newly made, the whole shows aggregate polarization in place of the crystal polarization. Besides this, aggregates and individual crystals are present which proves that the reaction goes over the solution.

The breaking up of the D hydroxide with the chloride is probably due to the fact that the chloride does not have the same crystal lattice as the D hydroxide, and because of this gives different aggregates. (Compare with Labanukrom).

2. The effect of acids on the different types of hydroxides is different from that of the salts, in spite of the fact that the first step in the reaction is the formation of a salt thru the dissolving of the hydroxide. The formation of the basic salt here is not in all cases localized on the gel, which is the starting point. The precipitation of the basic salt is out of the solution and according to the conditions, such as concentration of the acid, or ability to react and the accessibility of the oxide type, more or less close to the dissolved material.

For this reason, the treatment of hydroxide with sulphuric acid gives an instabile form of basic sulphate at first which changes gradually upon being in contact with the liquid. Two forms of basic sulphate minerals are known. They are said to differ only in their water content. They are Langite $3Cu(OH)_2.CuSO_4.H_2O$ and Brochantite $3Cu(OH)_2.CuSO_4$. Both crystallize in the rhombic system and have only slight crystallographic differences. (See Groth »Chemische Krystallographie« or Dana's »Mineralogy«.) The hardness and specific weight is a little less in Langit and it is probablly the instabile form. The instabile form which I observed from a B hydroxide had triangular or rhombic plates and aggregates formed to six-pointed stars and rosettes. This may correspond to the mineral Langite and can be replaced by the typical formation of the basic sulphate the spindles or the somatoids as they often appear in changing of a crystal type. (See figure.)

In the frozen gel C individual crystalls appear in the aggregate form of hydroxide in a characteristic disturbed form.

3. At the same time as the formation of basic salts, the appearance of a brown oxide gel is often noticed. The explanation of this is that the instabile A is dehydrated quicker to CuO than the change to basic salt. Quite noticeable is this on the stabile hydroxides C and D. This property gives a pointer on the mechanics of the formation of basic salts in these topochemical reactions.

The formation of brown oxide can probablly only be explained be this; that the hydroxides C and D by being in contact with cupric salt solutions, neutralizes the hydrolytically formed acid at first and makes reactive colloidal $Cu(OH)_2$ which changes gradually to CuO. The binding of the acid formed is alongside the hydroxide body and around this body a more concentrated solution is present from which the basic salt precipitates. The thickness of this layer depends upon the total concentration of the solution. For instance the basic sulphate is formed in a O.6N solution as granular aggregates, but in a N sulphate solution as a dense layer. Further from the bordering layer in the solution, after the acid, has been taken away, there is at first only a colloidal hydroxide, which changes to a loosely bound oxide gel surrounding the crystal.

3. The Effect of Different Metallic Salts on Copper Hydroxide.

Here our researches into single metallic salt mixtures or the insufficient addition of a neutralizing acid ended. By single metallic mixtures are meant mixtures in which there is only one metal in solution, as copper. Besides varying the form of the hydroxide the cation of the copper salts were varied as the nitrate, sulphate or the chloride. There is however another possibility, and that is to change the kind of metallic salt. These salts can be divided into two classes. The first in which the metal has greater electro-positivity than copper such as silver and mercury and those that do not have. Sabatier, A. Maihle and A. Recoura describe mixed basic salts of copper. These contain besides copper such metals as Hg'', Ag, Pb, Ni, Co, Cd, Fe''', Zn, and Al. Not all combinations described in the aforementioned researches were used by us. The following were selected by us: — Ni, Co, Cd, Zn. Trivalent elements were left out. The method of preparation was the same as with the copper salts. The four different types of hydroxide were treated with various concentrations of these salts at the ordinary range of room temperature.

In order to make clear the following paragraphs the general results of my observations are given here.

In judging the researches one must keep in mind that our purpose was to find systems in which characteristic morohpological appearances were observed. These were in combination with chemical changes. The sampling was therefore more on the surface of the subject than into the depth. Every individual research takes, because of the multitudinous appearances, more time than it was possible to give the subject for the time being. It is to be remenbered too that only after such researches have been made and clearness has been obtained, that certain cases can be selected for special study. These special studies can only be generalized after their relations to many cases and the conduct of these is known. Researches in this direction have obtained thru my studies.

Summarizing, the following is noticed: —

1. The effect of the different kinds of copper hydroxide, which was noticed in the single basic salts, is very similar in the reaction with other metallic salts. The effect decreases from A to D hydroxide quicker here than in the single salts. With A there is at first a gel-like »substituted« form, which either remains thus or changes to a more or less pronounced crystalline product. Characteristic forms are made with B, while the formation with C and D is influenced thru the compactness of of the material.

2. The effect of the concentration of the salt solution is very noticeable on A and B. The first step appears to be always a coagulation or conglomeration of the gel mass, which one can observe in increased dilution of the solution and in B in the secondary reaction. Generally the two reactions over-lap each other.

3. Corresponding to what Labanukrom found in his copper compounds with different anions and which I was able to verify in certain cases, there is also a large »flora« of typically formed bodies in the mixed basic salts. They would not have been sufficiently described, if they are only regarded as belonging to one crystal class or indentified only thru a combination of faces. One can observe specific individual crystals; more characteristic is the aggregate form of a combination. These can be a grouping of definite individual crystals or »somatoids«. Not only a change of the anion can change the form but also the cation of the other metallic salts.

The peculiar aggregate form of each system, which, is characteristic and can be easily reproduced, can be understood if the observations over their development, are followed in certain cases. This is true in the use of B (sometimes in A too) where the reaction is relatively slow.

The original sol of B coagulates thru the addition of a salt. This consists of rounded particles which hang together and keep their form remarkably well.

In these flake bodies the growth is in an isolated space of reaction (which can be compared with the growth by intussesception in cells) and the crystalline formation is made at the expense of the »cell« material in exchange with the reactive liquid.

The development of the crystal is controlled by the form and size of the field of reaction and is also determined by the crystallization ability or the solubility of the compound and the concentration of the salt solution. It was often found that the size of the typical aggregate form (see the Zn and Cd compounds) was the same size order as the coagulation units.

The growth of the thin-plated Zn and Cd compounds is to be explained with »layer lattices«. There is in the drop-like gel flake a direction which is most favored. Thru this favorism the whole structure is deformed and is under a tension, which rounds the surface. The following layers grow parallel and are under the effect of this tension of the whole structure and have to follow this change of space. Such forms can be seen in the photographs of our B hydroxide with $Zn(NO_3)_2$ or Cd (SO_4). Here several layers have been pushed against each other thru the tension, and opposite layers of particles are thus formed. In all these various changes the development of the aggregate is in the isolated space of the gel.

A further discussion of special cases is not given here. The idea was to present the principal that cause the formation of the characteristic aggregate form and which probably is of general importance.

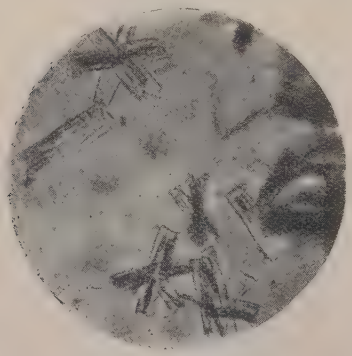
a) Copper Hydroxide and Nickel Salts.

Nickel Sulphate.

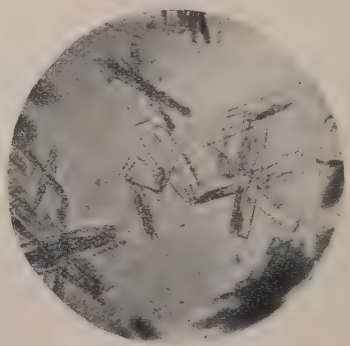
The A hydroxide gives with nickel sulphate solutions between 0.2N and 0.5N a uniform product under the microscope. They are all small needles without pyramidical ends, curving gradually together. As the concentration is increased towards 0.5N $NiSO_4$ they were more numerous and very slightly smaller.

The naturally aged B hydroxide or better said oxide shows only in one concentration (0.2N) forms that are similar to those in the hydroxide, and that is not uniform but mixed with some gel from the hydroxide. Another difference too was that the needles were not alone but also in clusters, each needle turned a little like a fan. In a concentration of 0.4N the product was

clear and large crystals were present when compared with the needles that had been noticed before. Their shape was a quadangular plate with lines parallel to the longer sides. Often the crystallization had been disturbed and the end may show a step-like formation; then too, another elongated form would grow on top, not completly parallel to the form that it had grown upon and also not completly finished. More remarkable was the fact that many of the crystals would so arrange themselves that three would cross each other, and give a six-sided figure. However this was not always the case sometimes only five arms were present. A change of $^{1}/_{10}$ in the $NiSO_4$ concentration did not give anything different from the lower concentration, as can be seen by the two photographs and drawing.



CuO in 0.5N $NiSO_4$
Magnified 720X.



CuO in 0.4N $NiSO_4$
Magnified 720X.

Drawing of product of
CuO in .05N $NiSO_4$ (600X)

These forms can easily be washed and a sufficient quantity was obtained to make a quantitative determination. From the percentage results obtained it can be seen that the product is not uniform.

	I		II	
Cu	30.71%		30.98%	
SO_4	26.96%		26.76%	
Ni	16.48%	22.31%	13.31%	12.71%

The amount of substance used to make a series (as I and II) was between 0.1 and 0.15 gms. The other two nickel determinations were especially made for nickel glyoxim. The copper was determined by electrolysis and the SO_4 as $BaSO_4$.

The frozen hydroxide C with 0.2N $NiSO_4$ partially changed, in the time that it was observed which was 10 days after mixing, to fine pointed needles clustered around and on a lump of frozen hydroxide. The width was slightly less than 27μ and the length 32μ. A better change was noticed in the 0.4N tube but the change here is only partial. The needles are clustered and once in a while alone. When they are clustered they are a attached to the surface of the frozen hydroxide. Their size is like that of the 0.2N. The following drawings will give an idea of the form of the needles.

Drawing of product of frozen $Cu(OH)_2$ in 0.4N $NiSO_4$ at 300X.

Drawing of product of frozen $Cu(OH)_2$ in 0.2N $NiSO_4$ at 300X.

The D »crystalline« hydroxide in the weakest concentration of 0.2N $NiSO_4$; it seems that some $Cu(OH)_2$ must leave the crystal as a gel. This taking out of some hydroxide is not just anywhere but lengthwise and the whole crystal breaks up. The new form appears as long needles. Some of these needles look almost like splinters of $Cu(OH)_2$ and micrometer measurements showed that their size was 13μ in length and 0.6μ in width. Very indistinctly there appeared to be trichites on the

ends of these needles. The next form, made with 0.4N $NiSO_4$, showed a great similarity to the form observed in the colloidal hydroxide at the same concentration. By a comparison of the drawings it will be hard to tell which is without the explanation at the bottom of each. The same thing was noticed in 0.5N $NiSO_4$ only more pronounced and the hydroxide was completely broken up.

Maihle gives in the mole and 0.5 mole solutions this formula:

$2NiSO_4.3CuO.12H_2O.$

CuO	31. %	31.5%	31. %
NiO	19.5%	19.45%	20.2%
SO^4	20.7%	20.6%	21. %

If the concentration is less, at 0.25 mole another formula:

$NiSO_4.3CuO.6H_2O.$

CuO	31.8%	31.6%
NiO	18.6%	18.5%
SO_4	18.8%	19.3%

Drawing, of product of »crystalline« $Cu(OH)_2$ and 0.5N $NiSO_4$. Large crystal 2X the others in size; i. e. 600X.

Nickel Nitrate.

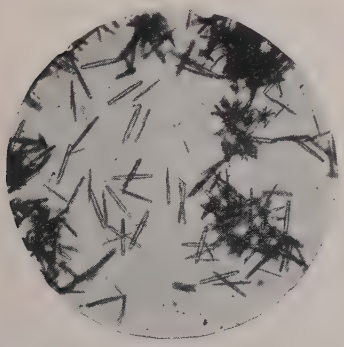
The A copper hydroxide was treated with concentrations of 0.25N to 1.6N $Ni(NO_3)_2$. It is impossible to describe the forms that resulted from the mixtures exactly. In the tube with the 0.25N $Ni(NO_3)_2$ the objects were rounded and occasionally elipsoidal. The diameter was measured and found to be 1.6μ. The maximum ability was noticed at 0.5N where the forms were oblong and at a magnification of 600X the length was 1.6μ and the width 0.8μ. Due to their small size it was hard to

define them exactly. That the length and width should have a ratio of 2:1 in this case, was due to the micrometer whose units were not smaller. Within a week in which all of these products of $Ni(NO_3)_2$ were examined the N and 1.6N solutions showed nothing but an indefinite brown smear under the scope.

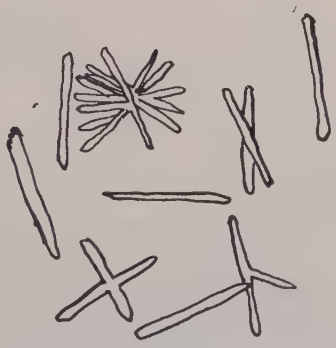
The B oxide showed greater ability to react and the forms were always longer than they were wide. Even at 0.25N the rectangular forms, which were in the center of a mass of brown

Rectangles in CuO and 0.25N $Ni(NO_3)_2$.
(Drawn from a magnification of 300X.)

oxide, had a length of 16.59μ and a width of 7.11μ. At 0.5N $Ni(NO_3)_2$ there is a slight differentiation into a rectangular form and a needle form. However the greater part of this tube was made up of a brown mass. The length of the rectangles was 33.18μ and the width 2.37μ. The N solution showed beside the brown gel multitudes of needles. These were either alone or crossed in groups of three or the ends over-lapped. The length of these individual needles was 9.48μ and the width 1.18μ. After a fortnight the brown gel had disappeared.



Product of CuO and N $Ni(NO_3)_2$ solution. Magnification 360X.

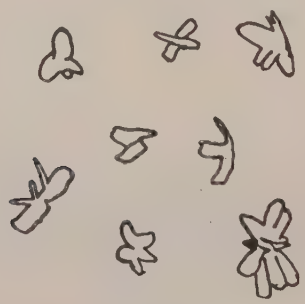


Drawing at 300XCuO and N $Ni(NO_3)_2$ solution.

The 1.6N solution showed what would appear to be two forms without any gel. They can both be called needle forms, one is broad and the other is narrow form. The measurements have shown that the narrow form is the broad one viewed edge-wise. The length is in both cases 16.59μ and the width of the broad form 33.55μ to 6.74μ and the width of the narrow form, i. e. the thickness, of the broad one is 1.18μ.

Drawing of product of CuO in 1.6N $Ni(NO_3)_2$ at 330 X.

The C hydroxide seems to have already the necessary form that the nickle nitrate can just enter to form the double salt with. The growth seems to be more by intussusception than by accretion. The whole irregularly shaped hydroxide breaks up into many small forms with 0.5N $Ni(NO_3)_2$. The length was 9.1μ and the width 5.2μ.



Drawing of product of frozen $Cu(OH)_2$ and 0.5N $Ni(NO_3)_2$ at 600X.

The case of a N solution of nitrate with the frozen hydroxide is a little different. The original form of the hydroxide is present and it is either made up of needles or is so covered with them that it gives the appearance of a fur covering. They are very fine and at a magnification of 600X their color was a blue green. The most concentrated solution of nickel nitrate used, was 1.6N. The outer form of the hydroxide was still present, after a week the color had become a brownish-green. The mass was just covered with irregular cleavages.

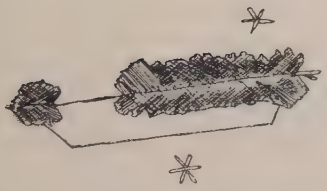
The D hydroxide was able to resist the 0.25N nickel nitrate solution and after a week nothing was noticed. The concentration which was just double that of the preceding showed unchanged

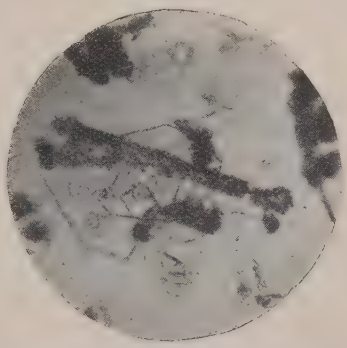
crystals and crystals where needles had grown on edges in a thick criss-cross position so matted together that a measurement of them was not an easy matter. The diameter of such a matted mass was 10.4μ. As could be expected the greater concentration, (N solution) increased the number of these needle masses on the crystals. They were then not only to be found on the edges or corners but over the broad surface of the hydroxide crystals. (See drawing and photograph.)

In this case Maihle gives this formula:

$Ni(NO_3)_2.3CuO.3H_2O$

CuO	49.6	49.4	49.6%
NiO	15.5	15.6	16. %
N_2O_5	21.4	21.4	21.3%





Drawing and photograph of the effect of 0.5N $Ni(NO_3)_2$ on »crystalline« $Cu(OH)_2$.
(Drawing 500X.) (Photograph 360X.)

Nickel Chloride.

Here we have, in all kinds of hydroxide used appearance of new forms. The existing material, whether it was colloidal or compact was the end form too. The hydroxide seems to be denser than it had been but no sharp defined or repeated form was observed. The color became a light blue which was different in color than the original material.

The oxide, which to begin with, was completely brown, changed its color in three days to a light blue gel. It did not show any forms in any of the concentrations used which were 0.2N; 0.4N; and 0.5N.

The frozen form retained its form in all concentrations. (See drawing.) There was a change in color to-wards a blue green shade. There can be two thoughts from this. Either some pressed hydroxide goes into solution and reacts with the nickel chloride or the nickel chloride enters into the pressed form. The first thought is not possible because there was no hydroxide or gel found either around or in the solution other than that which was in the pressed form. No other forms were observed either in the solution that could have been due to a wandering of any material from where it was. This seems to be a contradiction of the thought that reactions have to go over the solution. The chlorides in their behavior with copper have kept themselves in an exceptional form, that they do not give aggregates like the nitrates and sulphates.

Frozen $Cu(OH)_2$ in 0.5N $NiCl_2$
(Magnification 100X.)

The crystalline form did not differ from the preceding. It was not able to change even the color. Probably this was due to the reason that it was the most compact and arranged form that was used.

Maihle's formula in this compound is:

$NiCl_2.3CuO.4H_2O$

CuO	54. %	54.1 %
Ni	13.7%	13.6 %
Cl	16.3%	16.25%

b) Copper Hydroxide and Cobalt Salts.

Cobaltous Sulphate.

Working with the cobaltous sulphate we first noticed the greater activity of the oxide as compared with the hydroxide, both in the time that it required a reaction to take place and

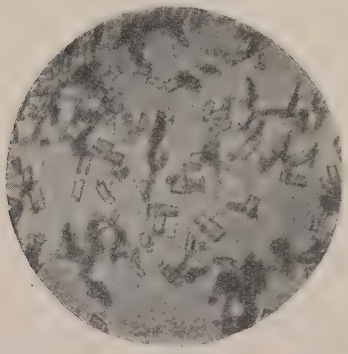
the size of the objects. The form that results from the mixing of hydroxide and the cobaltous sulphate depends first, on the concentration because different concentrations give several forms. Secondly, on the internal structure of the hydroxide, not taking into consideration the process of ageing, which is in no case exactly the same. One may wash the material out exactly the same number of times as the preceding and the other conditions remaining the same the difference can be noticed by the eye in the shade of the material. Of course a most decided factor is the ageing process. The hydroxide with the 0.2N $CoSO_4$ showed at first needles and some irregular material between. These needles are at first moderate in size but in a week they have become much smaller. Ten months later these needles were very small. The 0.4N solution of $CoSO_4$ showed not exactly needles because the ends were square i. e. they were out off sharply and not tapering into a point as the needles. The material was not clear, but in four days large rectangular forms appeared and the material was free of any other forms. At 0.5N $CoSO_4$ the solution was made up of rods and needles but a later observation of eight months showed only rods.

The oxide reacted in a 0.2N $CoSO_4$ solution that very fine needles were present at first and later rectangular plates were also present. Many were the forms that were at first present

Drawings of objects found CuO in 0.4N $CoSO_4$.

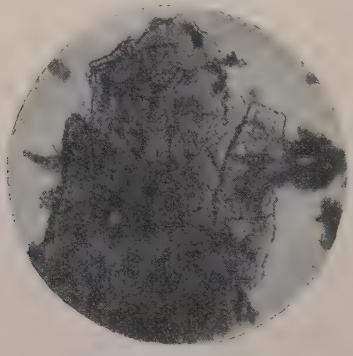
in the 0.4N $CoSO_4$. Besides the rectangles needles were and some ovals. Leaving this material stand for several months the rectangles remained and another form apppeared (see drawing). The rectangles were not complete all around but had one corner cut into as can be seen on the photograph or were in a cluster. The 0.5N solution showed no needles but benzol ring shaped forms, rectangles and rods. The rectangles showed the greatest perma-

nance. Having had some very old oxide which had stood over a month we treated it with a 0.5N solution and it showed regular hexagonally sided figures which were present even upon a later observation.



Product of CuO in 0.4N $CoSO_4$.
Magnified 720X.

The frozen hydroxide in the weak solution of 0.2N, there were things to be seen. Besides some gel, which could have been besides the copper hydroxide, cobaltic hydroxide, there were some rectangles with truncated corners alone but often in groups. They were very thin but large, measuring 72.9μ in length and 10.8μ in width. The next concentration (0.4N) was totally different. To begin with the compact form of the frozen material was still there but it had become brown. On this brown material (not in it as was observed by focusing sharply) were rectangles. These could easily be seen with the low power objective and the length varied a little but one was found to be 31.2μ and the width 15μ. (See photograph and drawing.) There was nothing new to notice in the next tube with a concentration of 0.5N; its forms were like those in 0.4N.



Rectangles of frozen $Cu(OH)_2$ in 0.5N $CoSO_4$.
(Magnified 360X).

Drawing of rectangles on frozen $Cu(OH)_2$ in 0.4N $CoSO_4$. (Magnification 100X.)

The »crystalline« hydroxide form was broken up a great deal in the 0.2N solution of $CoSO_4$ and some had become a brown gel and some was still unchanged in color or form. Besides this quite a few triangles were present which had on one side a slight bump. With the 0.4N $CoSO_4$ there were many needles, long and thin, some gel and some heavily etched hydroxide. The 0.5N $CoSO_4$ solution showed only a brown gel and some unchanged crystalline hydroxide but no other forms were present.

Maihle's formula for this salt is like that for nickel. In the molecular and 0.5 solution it is

$$2CoSO_4.3CuO.12H_2O$$

CuO	31.8%	31.6%
CoO	19.3%	19.5%
SO_4	20.5%	21.1%

However in a $^1/_4$ mole solution it is:

$$CoSO_4.2CuO.6H_2O$$

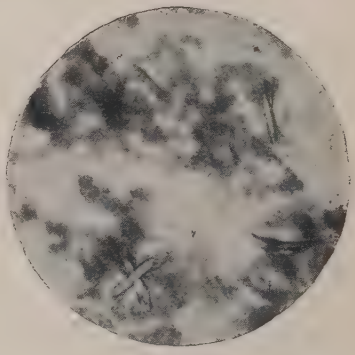
CuO	37.4%	38. %
CoO	18. %	17.7%
SO_4	20. %	20.2%

Cobaltous Nitrate.

A. The hydroxide in a solution of cobalt nitrate with a normality of 0.25N showed only some oblong shapes, none of which could be defined. The micro color was brown and as the concentration of the nitrate increased, the color of the precipitate became deeper towards a purple. The shapes were less pronounced as the concentration increased until in a N solution only a gel-like material was noticed.

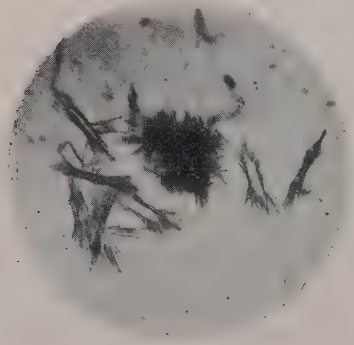
B. The oxide was however totally different from the hydroxide. Long needles with many trichites on the side were noticed in the 0.25N solution along with a great quantity of gel. These needles were measured and their size was, exclusive of the hair-like protuberances, 7.11μ in width and 35.5μ in length. (See

photograph and drawing.) The next tube with a concentration of 0.5N $Co(NO_3)_2$ was the same as the less concentrated one; the amount of gel to the needles being about 50%. The normal solution was again different from the others. The needles were



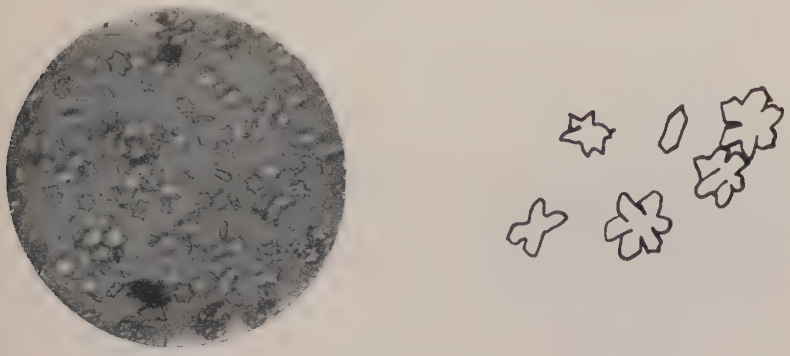
Drawing (330X) and photograph (360) of product of CuO and 0.25N $Co(NO_3)_2$.

about the same in outer form as the 0.25N and 0.5N solution but they did not have any trichites and were alone, also the amount of gel was less. They were measured and found to have a length of 5.5μ and a width of 1.1μ. The most concentrated of our solutions was 1.6N $Co(NO_3)_2$. These objects, besides being alone would often be twinned and have a center that three would give the appearance of an asterisk. Such a form would a diameter of 8.8μ. The edges of these forms were not sharply angular and the measurements of the single ones was 8.8μ in length (same as the diameter of the asterisk form) and the width 3.3μ. (See photograph and drawing.)



Photograph of needles in 0.5N $Co(NO_3)_2$ and CuO. (Magnified 720X)

C. Regarding the frozen hydroxide from the weakest solution 0.25N to the strongest 1.6N, one has a continous decrease in size of the particles. Already in the last two they are so small that they could not be exactly defined. However in all, the hydroxide remains where it was and does not break up.



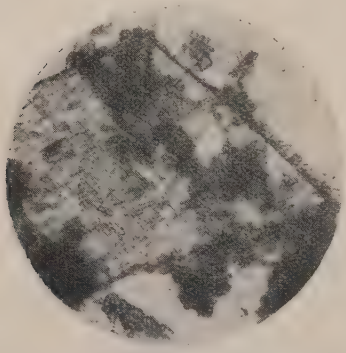
Drawing and photograph of forms in CuO and 1.6N $Cu(NO_3)_2$
(Magnified 600X and 720X respectively.)

In the weakest concentration and weakest form, the needles seem to be on top of the hydroxide. Their size was measured as being 7.8μ in length and 1.3μ in width. In the next tube (0.5N) the aggregates were shorter than in tube 0.25N $Co(NO_3)_2$ but wider, giving them more of an oval appearance. In the next two tubes, N and 1.6N no measurements could be made and the color of the hydroxide, if it was still hydroxide, was brown.

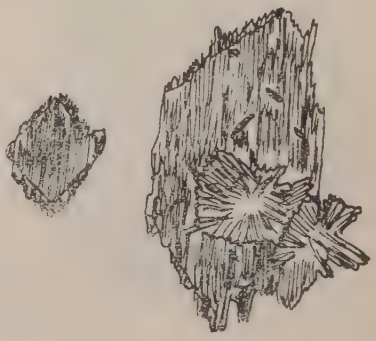
Drawing of needles in 0.25 N $Co(NO_3)_2$ and frozen $Cu(OH)_2$
(Magnified 600X.

D. The crystals of hydroxide in the 0.25N $Co(NO_3)_2$ solution have broken up into a smaller needle form. These have grouped themselves into clusters around a point. Besides having a blue

color their size was measured and found to be 0.7μ in width and 10.4μ in length. The next concentration of 0.5N $Co(NO_3)_2$, the large crystals that one had to start with had not broken up. Over the surface and at the edges can be seen either needles or rounded cluster-like forms. The color in both cases was blue. (See drawing and photograph.)

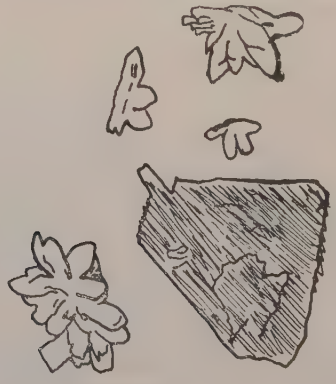


Crystalline $Cu(OH)_2$ and 0.5N $Co(NO_3)_2$. (Photograph 720X.)



(Drawing 500X)

Already in the normal solution there was besides a lengthwise lineation on the surface of the crystalline hydroxide, also, separated from the crystalline hydroxide rounded cluster-like forms. (See drawing.) These last mentioned »somatoids« were blue in color and can easily be seen in the drawing. The most concentrated solution which was used (1.6N) had the lengthwise lineation without any loss of the form of the hydroxide. Not all



Crystalline $Cu(OH)_2$ in N $Co(NO_3)_2$ (Drawing made from 600X.)

the crystals had these lines, some were completely free of any attack. Instead of the somatoids as they were described in the normal solution only needles were observed.

The formula given by Maihle is:

$$Co(NO_3)_2 . 3CuO . 3H_2O$$

CuO	49.6	49.5	49.5%
CoO	15.5	15.5	15.6%
N_2O_5	21.4	21.4	21.2%

Cobaltous Chloride.

It has been brought to the attention before that the chlorides do not react with great facility in forming compact forms. In the forms of the hydroxide that show a higher degree of dispersion i. e. the colloidal hydroxide and the aged product, nothing was observed but a light purple color with a slime. This color is probably due to the combination of the blue and red of the copper and cobaltous ion. On the compact forms the effect was negligible. The frozen form showed a great number of fissures and the color in all cases was a pronounced green. Only in the most concentrated solution which was 0.5N $CoCl_2$ did the edges appear to be breaking up a little after two days. The crystalline hydroxide was not affected by the chloride after a week in a 0.2N and 0.4N solution. The next test with 0.5N $CoCl_2$ showed in the same time a few specs of gel, but the crystals seem to be otherwise intact. A later observation showed that the form had been lost leaving only a brown gel in rounded groups.

The formula for this salt according to Maihle is:

$$CoCl_2 . 3CuO . 4H_2O.$$

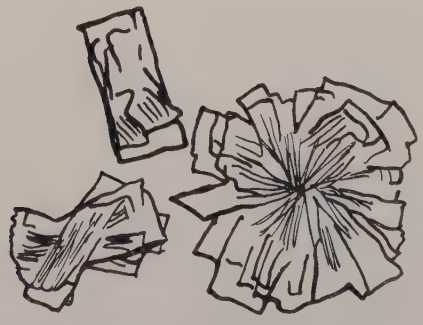
CuO	53.3%	53.6%
Co	13.8%	13.7%
Cl	16. %	16.1%

c) Copper Hydroxide and Zinc Salts.

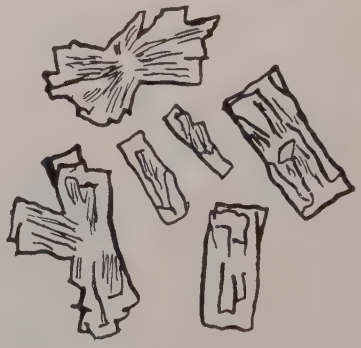
Zinc Sulphate.

The blue hydroxide was treated with zincs ulphate in solutions which varied between 0.33N and N and were left at ordinary temperatures, and not as A. Recoura at 75°C. Between 0.4N and 0.6N the conditions in the solutions must have changed to cause an aggregation in a cluster form with some gel and those below 0.4N were a light blue gel. Both 0.33 and 0.4N $ZnSO_4$ remained the same for a period of nine months. The 0.6N showed the first clusters, which were mixed with a gel. These clusters were made up of rectangular plates one on top of the other and slightly turned. These were not twinned to any particular plane nor were the arms any repeated number or angle. Some of these rectangular plates were observed in the 0.75N and N solutions alone besides the grouped type and gel. The color was a light blue in all cases.

The oxide changed in the weakest concentration of 0.33N $ZnSO_4$, and although it was not possible to say with certainty what the form was, it was probably needles. In the 0.4N with the hydroxide we did not have the rectangularly plated clusters but with the oxide there was besides the gel, rectangles alone or in groups. The same thing that was said of 0.4N can be applied to the following concentrations and in the N solution the form was the same as in the weaker. (See drawing.) Generally speaking an increase in the concentration would increase



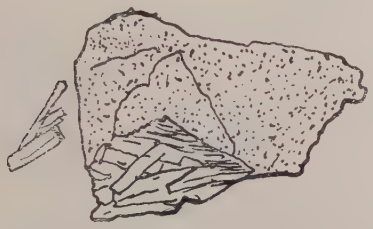
Forms found in N $ZnSO_4$ with CuO
(Drawing from 333X.)



Forms found in N $ZnSO_4$ wih CuO
(Drawing 333X.)

the affect of a substance. After having added the frozen hydroxide to the 0.6N solution of $ZnSO_4$ and letting the mixture stand for ten days the original form was still present but a splitting up into very minute needles was noticed. These needles were held together thru a sort of smear. The next concentration (0.75N) showed besides these minute forms some frozen material that had not been changed. The normal solution showed no outward change in form only that the color was a slightly darker shade of green than the original material had been.

The crystalline form broke up in all the concentrations of the sulphate and changed to a light blue colored smear. In this material was found, in the 0.6N concentration, a few rectangular clusters as they were drawn. The material was observed after having stood ten days.



Form observed in 0.6N $ZnSO_4$ and crystalline $Cu(OH)_2$ (Drawing made from 300X.)

Here Maihle gives two formulas where the Cu and the Zn change places. Where there is a $^1/_2$ molecule of $ZnSO_4$ per liter it is:

$$2ZnSO_4 . 3CuO . 12H_2O.$$

CuO	30.4%	31. %
ZnO	20.8%	20.5%
SO_4	20.8%	20.5%

The other formula is:

$$2CuSO_4 . 3ZnO . 12H_2O.$$

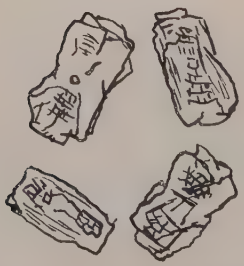
CuO	21. %	20.8%
ZnO	30.6%	31. %
SO_4	20. %	20.8%

The concentration here was between 2 and 3 mole per liter.

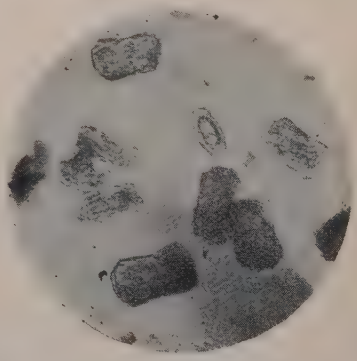
Zinc Nitrate.

A. The resulting product from a mixture of hydroxide in 0.4N $Zn(NO_3)_2$ was in a week's time an irregular very fine form which at 600X appeared to be dots. The macro color was blue and under the microscope it was brown. In the next tube with a concentration of 0.8N $Zn(NO_3)_2$ the statements applied to 0.4N can be used here. In the 1.6N solution the forms were a little larger than the preceding and irregular like rods and circles. The macro color was blue and the micro brown. The next test tube was no better than the former. Here thru concentrations that varied from 0.4N to 2N no change was noticed.

B. The oxide reacted in as short a time as three days but there was plenty of gel present with the rectangular scaly form. Ten days after this observation the gel had disappeared and the forms were well defined. The micrometer measurements showed a length of 45.03μ and two widths which may be taken as due to two crystals lying one on top of the other without covering each other. The widths were 28.44μ and 23.7μ. From the photograph and drawing a very good picture of them can be had. The forms appear to be placed one on top of the other and each succeeding one is turned a little, giving the appearance of a pack of cards which had been twisted slightly and that each layer is a little smaller than the lower. When they break their fracture is both longitudinal and transverse. The next concentration of 0.8N $Zn(NO_3)_2$ showed no gel after 3 days. The

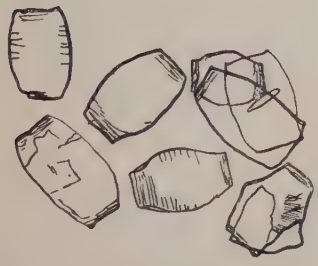


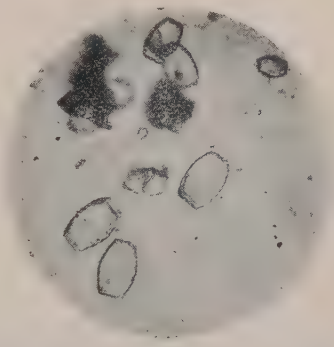
Product of CuO in 0.4N $Zn(NO_3)_2$. Drawing from 300X.



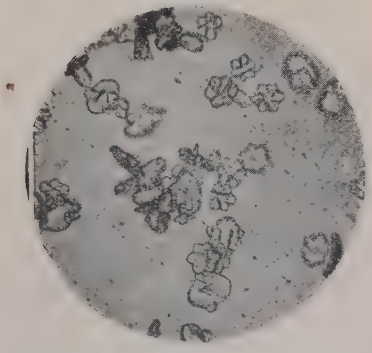
Form found in 0.4N $Zn(NO_3)_2$ and CuO. (720X.)

forms were totally different from the rest. These were barrel shaped and had varying lengths of 27.3μ to 32.5μ and widths of 16.9μ to 19.5μ. They darkened polarized light four times upon a rotation of 360°. They were banded like a hoop. (See drawing and photograph.) The next tube with 1.6N $Zn(NO_3)_2$ had totally different forms than the preceding. Already in three days it was free of gel and showed rose-like flat forms which, besides being affected by polarized light four times, showed that their size was 19.5μ in length and 13μ in width. These were rounded forms and the greater number were alone. The 2N test tube showed the same type of forms as the 1.6N tube, but they were more clustered and sometimes even star-shaped. (See drawings and photograph.)





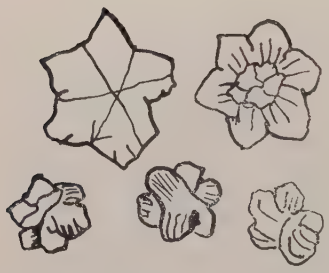
Barrel shapes found in 0.8N $Zn(NO_3)_2$ and CuO. Drawing 600X. Photograph 720X.

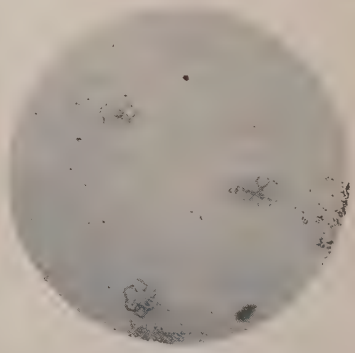


Forms found in CuO and 1.6N $Zn(NO_3)_2$

(Drawing 600X.) (Photograph 720X.)

C. The frozen hydroxide kept its form for ten days in the 0.4N $Zn(NO_3)_2$; the color was however darker on the edges of some of the pieces where there was some amorphic to semi-needle like growths. The 0.8N $Zn(NO_3)_2$ solution was the same as the preceding. In the 1.6N solution, besides the still present forms of the hydroxide, were noticed very few rather long needles, which had a length of 37.8μ and a width of 8.1μ. In the 2N solution not a needle was found only the form of the frozen hydroxide. The macro color was blue.





Types found in 2N $Zn(NO_3)_2$ and CuO.
(Drawing 600X.) (Photograph 720X.)

D. The crystalline hydroxide was not attacked by a 0.4N solution of $Zn(NO_3)_2$ in eight days. The 0.8N solution was able to make itsself felt on the surface of crystals in a lengthwise lineation. Besides this, in the solution, there were found two star »somatoids« which were like those found in the 1.6N solution of the oxide. The 1.6N solution etched the surface of the crystalline hydroxide in a longitudinal direction and the crystal was surrounded by a veil of an irregular gel. A later observation showed that these star »somatoids« were increasing and growing on the surface.

The zinc nitrate has this formula according to Maihle:

$$Zn(NO_3)_2 . 3CuO . 3H_2O$$

CuO	49.%	49.1%	49.3%
ZnO	17.%	16.7%	16.9%
N_2O_5	20.%	20.9%	20. %

Zinc Chloride.

Here we come again to a chloride and from what has been noticed before, here we can expect nothing but a colloidal mass. Such were our expectations and they were fulfilled. Having observed the chlorides of Co, Ni and the mixture of copper and HCl and always getting the same effect, the reason for this is to be sought in the chloride ion and not in the other component.

The hydroxide showed no forms in the zinc chloride solutions with a normality of 0.4; 0.8; and 1.6. The gel that was formed was a very light blue. In the 2N solution there were a number of forms present but these had the form of a pure basic chloride of zinc.

The oxide changed upon mixing it with solutions of zinc chloride between 0.4N and 2N to a light blue gel with a few indefinable specs present. These had a diameter of less than a μ.

The zinc chloride is a substance which when in solution has the tendency to form a basic salt. The frozen hydroxide is a heavy material which settles easily. Upon observing the test tubes with frozen hydroxide after a week showed in all two layers regardless whether it was in the 0.4N solution or a 2N solution. The lower layer was a blue from unchanged hydroxide and above a mass of white dots enclosed in a white slime. Two thoughts can be taken here either the water in the test tubes caused the hydrolysis or some copper hydroxide went into solution and reacted with the zinc chloride. Our solution of zinc chloride had a normality of 4N to start with and was clear. It was mixed with a watery solution of hydroxide in such a quantity as to bring it to the desired normality. Even in the 2N solution we had the basic chloride of zinc which is already such a strong solution that hydrolysis should not play the same role that it did in the weaker solutions. In all of these solutions copper hydroxide was present and also in all tubes basic zinc chloride so that the formation of this basic zinc chloride can only be explained thru some of the copper hydroxide going into solution no matter how little it may have been.

In the tubes that the crystalline hydroxide was mixed with zinc chloride a decrease in the intensity of the color was noticed as the concentration increased. In the 0.4N tube there was a mass of blue colloid. Dispersed in this mass were rectangles with a length of 29.3μ and a width of 15.6μ. These rectangles may have been only basic chloride. The next concentration of 0.8N did not disintegrate all the crystalline hydroxide, which could be seen in the fine light blue mass. No forms were present and no unattacked crystals in the 1.6N but a few in the 2N. No forms with definite outline were found in either.

Maihle's formula is:

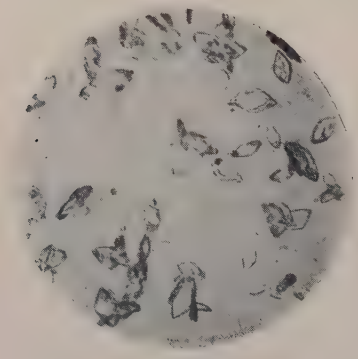
$$ZnCl_2 . 3CuO . 4H_2O$$

CuO	52.8%	52.9%
Zn	15. %	15. %
Cl	16.5%	16.3%

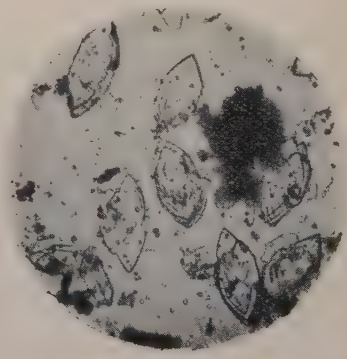
d) Copper Hydroxide and Cadmium Salts.

Cadmium Sulphate.

The hydroxide gave forms that were rounded diamond shaped which did not change in several months, and was clear of gel. These rounded diamonds from the 0.3N solution showed on the surface the growth of other individuals as can be seen



$Cu(OH)_2$ with 0.3N $CdSO_4$
Magnified 720X.

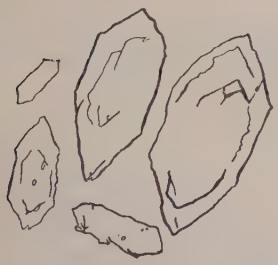


CuO with 0.3N $CdSO_4$
Magnified 720.

in the drawing. Both the 0.6N and the 0.85N $CdSO_4$ solutions showed the same form as those in the 0.3N tube. One exception was that those in the 0.85N $CdSO_4$ did not have the lines on the top as the others. Both the 1.2N and 1.5N solutions showed only a brown gel even at a magnification of 1500X.

Drawing of forms in $Cu(OH)_2$ and 0.3N $CdSO_4$. (600X.)

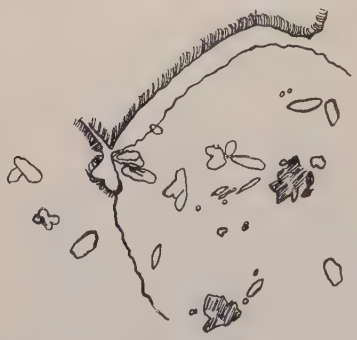
As has been said, the hydroxide gave rounded pear to diamond shaped forms the oxide gave much more angular forms and more of the six-sided benzol ring type. (See drawing and photograph.) On their surfaces there were growths of smaller but similar individuals. What has been said of the 0.4N solution holds true in the 0.6N solution and that in five months the amount of gel became less. In the 0.85N solution starts the



Forms in CuO and 0.3N $CdSO_4$. (Drawing 600X.)

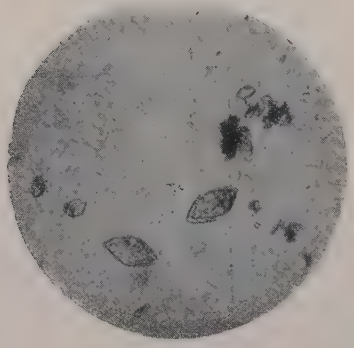
building up and tearing down process. The aggregates are large and clear but often appear to be eaten away on an edge. The next tubes in which there was no hydroxide showed that they were getting more pear shaped and also deeply pitted.

Upon observing the frozen hydroxide with the 0.3N $CdSO_4$ after ten days, the hydroxide was made up, of an ovals, nevertheless the hydroxide was able to keep its contour. (See drawing and photograph.) The measurements made showed that they had a length of 6.5μ and a width of 2.6μ. The next concentration of 0.6N $CdSO_4$ showed again a marked similarity to the forms noticed with the hydroxide and oxide. The ends were sharp and the rest had more of a gradual contour. The lamellar structure was also noticed where each succeeding form was smaller than its predecessor. Remarkable in the measurements was the fact that the ratio of length to width was exactly



Frozen Hydroxide in 0.3N $CdSO_4$. (600X.)

2 : 1. The width was measured and found to be 16.2μ and 18.9μ on certain forms and the length 32.4μ and 37.8μ. In the 0.85N solution some gel was present besides the large diamond shaped aggregates which were just described. Two aggregates



Frozen $Cu(OH)_2$ in 0.85 $CdSO_4$. (Magnified 360X.)

were actually found embedded in the still present frozen hydroxide. The size of the aggregates were found to be 64.μ in length and 32.4μ in width. This is again a ratio of 2:1.

In the 1.2 N tube this gel was increasing; the aggregates were the same in size and form as in the preceding tube. In the tube with a concentration of 1.5N $CdSO_4$ the thought is that the reaction goes over the solution. Besides the increasing amount of gel the old frozen hydroxide seems to be washed out and along side the aggregates can be seen. There are now only a few such forms but a great quantity of gel. The length was 32μ and the width 16.2μ.

The crystalline hydroxide was not much affected by a solution of $CdSO_4$ in four days. In all the tubes the crystals were etched slightly but otherwise they were as before.

In Maihle's work this formula is given:

$$2CdSO_4 . 3CuO . 8H_2O$$

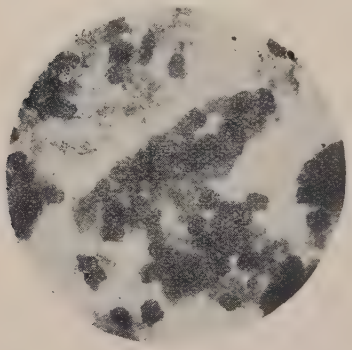
CuO	30. %	30.4%
CdO	33.8%	34. %
SO_4	21.1%	20.8%

Cadmium Nitrate.

A. The hydroxide which had been in contact with various solutions for six days before the first observation was made, showed that below a normal solution the gel had a beautiful sea-blue color but no forms. In the N $Cd(NO_3)_2$ small forms were noticed. They appeared to be polygons with the width and length the same, which was 4.4μ. Whether the objects found in 1.6N $Cd(NO_3)_2$ were globules or angular bodies could not be determined. They measured 1.1μ in diameter.

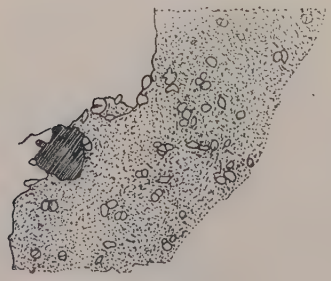
B. The oxide did not show anything but a brown gel in the 0.25 $Cd(NO_3)_2$ after having had them together for a week. The next tube with 0.5N $Cd(NO_3)_2$ showed a very compact mass

of very small specs, in another brown material. The next tube with the N solution was better. Very noticeable was the regular almost rectangular position of the gel on the object glass and the sprinkling of these specs, which were much like Malacite throughout the gel. The size of these specs was measured as having a diameter of 24.3μ and 18.9μ. (See photograph.)



CuO and N $Cd(NO_3)_2$ (360X.)

C. As the concentration of the cadmium nitrate increases, the products that were observed in the frozen hydroxide became smaller. In the 0.5N $Cd(NO_3)_2$ the little ovals were right in the midst of the gel. (See drawing.) These ovals which have a line through them had a length of 5.2μ and a width of 3.9μ. With the N $Cd(NO_3)_2$ they were smaller and less than before. In the 1.6N solution they were still present in the gel and had a diameter of 1.3μ.



Frozen $Cu(OH)_2$ and 0.5N $Cd(NO_3)_2$ (600X.)

D. In the 0.5N $Cd(NO_3)_2$ and the crystalline hydroxide were noticed little rods all over the surface of the crystal. These were measured as having a length to width ratio of 2:1. The length was 2.6μ and the width 1.3μ. The first observation was made in three days and after a week they had not changed. The normal solution showed that the increase in concentration rounded the forms a little. They too were found on the surface of the crystal without any point being especially favored by them.

The composition here is, according to Maihle:

$$Cd(NO_3)_2 . 3CuO . 3H_2O$$

CuO	42. %	41.6%
CdO	22.4%	22. %
N_2O_5	18.5%	18.3%

Curriculum vitae.

Ich, William Auguste Endriss, wurde in Philadelphia, Pa., U. S. A., am 18. Februar 1903 geboren. Ich besuchte vom September 1909 bis Juni 1917 die »Newton Grammar School«, Philadelphia und nachher die »West Philadelphia High School for Boys« und absolvierte dort den »academic course« im Juni 1921. Im Sommer bestand ich die psychologische Aufnahmeprüfung der »University of Pennsylvania«, zog aber dann nach Bern, wo ich an der Universität Bern vom Oktober 1921 bis Juli 1923 studierte. Ich reiste zurück nach Amerika und hörte die Vorlesung der »Philadelphia College of Pharmacy and Science« für zwei Semester zu. Dann kehrte ich im Oktober 1924 wieder nach Bern zurück und studierte weiter an der Universität Bern bis auf den heutigen Tag, den 29. Januar 1929.

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